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Orientational ordering of commensurate $Fe(CO)_5$ monolayers on graphite

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Elastic neutron diffraction and Mössbauer spectroscopy have been used to study the structure, orientational-disordering (OD) transition, and melting of an $Fe(CO)_5$ submonolayer adsorbed on Grafoil. The OD transition occurs between 150 and 167 K from a two-sublattice $(\sqrt{7}\times\sqrt{21})$ structure to a nearly $(\sqrt{7}\times\sqrt{7})$ phase in which the molecules are believed to rotate about the surface normal. Mössbauer spectra exhibit a more abrupt variation with temperature near melting at 170 K than through the OD transition.

Recently, there has been increased interest in physisorbed monolayers of *nonspherical* molecules on graphite.[1,2] In contrast to rare gases which are known to condense in hexagonal layers, little is known of the monolayer structure of these molecules—particularly their orientational ordering. Moreover, such films exhibit phase transitions which do not occur in monolayers of spherical atoms. One of these is the orientational-disordering (OD) transition to a phase in which there is long-range translational order but in which each molecule rotates at its equilibrium site. Experimental evidence of OD transitions has been found for nitrogen[1,3] and ethane[2,4] monolayers on graphite, and they have begun to be investigated theoretically by computer simulation.[5,6] The computer models assume the molecular centers to be fixed at their lattice sites and for rotation to occur about an axis perpendicular to the surface. Depending on lattice symmetry and intermolecular interactions, both first order[5] and continuous[6] OD transitions have been predicted.

We have recently begun to study the structure and phase transitions of iron pentacarbonyl [$Fe(CO)_5$] monolayers on graphite. This bipyramid-shaped molecule was selected because it is favorable for structural investigations by neutron diffraction while it can also be probed dynamically by Mössbauer spectroscopy.[7,8] We describe here a model for the $Fe(CO)_5$ monolayer structure at low temperatures inferred from neutron diffraction and show it to be consistent with calculations based on empirical atom-atom potentials. We then present evidence from both neutron and Mössbauer experiments for an OD transition between 150 and 167 K followed by melting at 170 K. We find the complementarity of neutron diffraction as a probe of orientational order and Mössbauer spectroscopy with its sensitivity to translational motion of the adsorbed molecules to be very useful in developing a model of the OD transition.

The neutron scattering experiments were performed at the University of Missouri Research Reactor Facility on a two-axis spectrometer (wavelength $\lambda=4.07$ Å) equipped with a five-counter multidetector-data acquisition system.[9] The Mössbauer spectrometer located at the Technion was operated in a constant acceleration mode and used a 25-mCi Rh:^{57}Co γ-ray source.[10] Both neutron and Mössbauer samples consisted of a Grafoil[2] substrate having a surface area of ~ 20 m^2/g. The neutron sample was oriented with the scattering vector $\vec{Q}$ parallel to the foil planes while in the Mössbauer experiments the gamma $\vec{k}$ vector ($\vec{k}_\gamma$) could be either parallel or perpendicular to the foils.

The neutron-diffraction patterns from a 0.9-layer $Fe(CO)_5$ film are shown as a function of temperature in Fig. 1. They have been corrected for background scattering from the Grafoil substrate.[11] Little change is observed in the patterns as the temperature is raised to 125 K. To solve the low-temperature structure, we proceeded as follows. The most intense Bragg peak at $Q=1.11$ Å^{-1} ($d=5.64$ Å) could be indexed as the first reflection of a $(\sqrt{7}\times\sqrt{7})19°$ superlattice on the graphite basal plane. However, higher-order peaks labeled (12) and (41) at the bottom of Fig. 1 were not permitted by this unit cell. As suggested by the herringbone structures found for com-

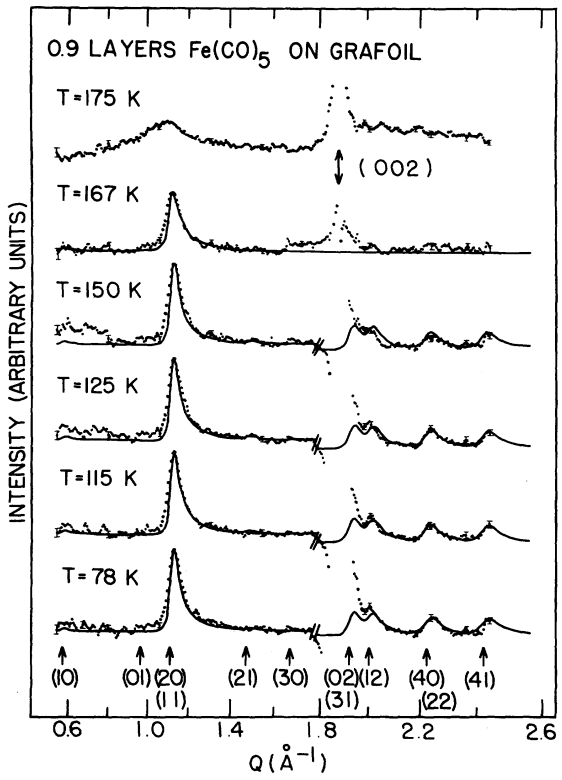

FIG. 1. Temperature dependence of the neutron-diffraction patterns from a 0.9-layer $Fe(CO)_5$ film adsorbed on Grafoil. The intense scattering near $Q=1.9$ Å^{-1} results from imperfect background subtraction near the graphite (002) peak. The solid lines for $T \leq 150$ K are the diffraction profile calculated for the monolayer structure illustrated in Fig. 2. The profile calculated at 167 K is for a nearly $(\sqrt{7}\times\sqrt{7})$ commensurate lattice in which the molecules are rotating about an axis perpendicular to the surface as described in the text.

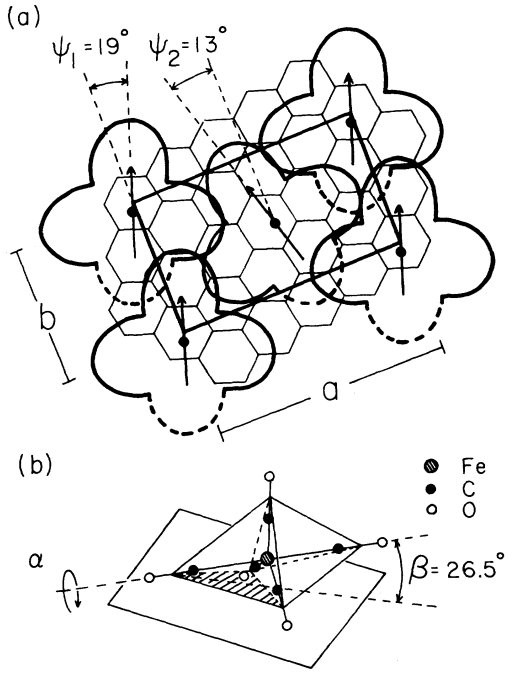

FIG. 2. Structure of the $Fe(CO)_5$ submonolayer. (a) Projection on the graphite basal plane. The $(\sqrt{7}\times\sqrt{21})19°$ unit cell ($a=6.51$ Å, $b=11.27$ Å) is drawn with its corners at the center of a graphite carbon hexagon. Molecules are outlined by approximate van der Waals radii (dashed line at end of molecule indicates CO group further from the surface). Arrows are projection of molecular principal axis through the Fe atom (●). (b) Orientation of molecule relative to surface (face-parallel configuration).

mensurate N_2 (Refs. 1 and 3) and ethane[2,4] monolayers on graphite, we then considered models composed of two $(\sqrt{7}\times\sqrt{7})$ sublattices corresponding to the $(\sqrt{7}\times\sqrt{21})$ rectangular cell in Fig. 2(a). The Bragg peak positions for this cell are indicated by arrows labeled by their Miller indices at the bottom of Fig. 1. All of the observed peaks are now predicted, although several allowed reflections are too weak to be detected.

After finding a unit mesh for the monolayer, we then determined the orientation of the two molecules in the unit cell by analyzing the relative intensity of the Bragg peaks observed. Since multiple-scattering effects are negligible, the peak intensities can be computed directly from the geometrical structure factor of the monolayer. A profile analysis technique described previously[4,12] based on a modified Warren line shape[13] was used to fit the polycrystalline monolayer diffraction pattern. The three Euler angles of each molecule, α, β, and ψ defined in Fig. 2, were varied systematically to obtain the best fit to the diffraction pattern at 78 K shown in Fig. 1.[14] The fit assumes a unity Debye-Waller factor and yields a coherence length[13] $L=120$ Å in the film.

The monolayer structure which we have deduced is illustrated in Fig. 2. The molecules lie in a herringbone pattern with one face of their bipyramid structure parallel to the surface as in Fig. 2(b). We estimate an error of about $\pm 5°$ in the angles α and β which determine the orientation of the pyramid face relative to the surface. The calculated profile is more sensitive to the angle ψ between the projection of the principle axis of the molecule on the surface and side b of the unit cell. We can exclude the case $\psi_1=\psi_2$ so that there is no glide line parallel to the side b. We also find that the fit can be improved if the second molecule is displaced slightly from the cell center with its center of mass (Fe atom) at the point $(0.52a, 0.48b)$ measured from the lower left corner of the cell in Fig. 2(a).

Analysis of the neutron-diffraction pattern does not give the position of the monolayer unit cell relative to the graphite basal plane. In Fig. 2(a), the molecule at the cell corner has been placed at the site

which we calculate from empirical atom-atom potentials to be most favorable for a single molecule on a basal plane surface.[15] The Fe atom is at the point $(-0.01a, -0.06b)$. We have also performed calculations with an 18-molecule cluster[10] similar to those in Ref. 12 but which include both substrate and intermolecular interactions. We find that, to within the calculational uncertainties, all of the molecules have the face-parallel configuration of Fig. 2(b). If the corner molecule is fixed at its site in Fig. 2(a), the center of mass of the second molecule is found to be at the point $(0.54a, 0.46b)$ with $\psi_1 = 16°$ and $\psi_2 = 13°$. This configuration agrees with that inferred from profile analysis of the diffraction patterns ($\psi_1 = 19°$ and $\psi_2 = 13°$) to within experimental error.

As shown in Fig. 1, the diffraction patterns begin to change at temperatures above 125 K. A decrease in the intensity of the higher-order Bragg peaks is just discernible at 150 K. By 167 K, they have disappeared entirely leaving only the first peak shifted slightly to lower Q. We interpret these changes as resulting from a transition to an orientationally disordered phase in which the molecules occupy a hexagonal lattice nearly $(\sqrt{7} \times \sqrt{7})$ commensurate with the graphite basal plane. The profile fitted to the diffraction pattern at 167 K assumes the molecules to be in the face-parallel configuration of Fig. 2(b) and to be rotating about an axis perpendicular to the surface passing through the Fe atom.[16] As observed, the higher-order Bragg peaks are predicted to be absent. The fit to the remaining peak yields a lattice constant which is 1.5% larger than required for $(\sqrt{7} \times \sqrt{7})$ registry and a decrease in the coherence length to $L = 80$ Å. The model also predicts this peak to have the same intensity as in the low-temperature herringbone structure. From Fig. 3(a), we find a 25% decrease in the integrated peak intensity between 150 and 167 K. This decrease may result from a Debye-Waller factor contributed by translational motion coupled to the sterically hindered molecular rotation.

In contrast to the neutron-diffraction patterns, we have found considerable temperature dependence of the Mössbauer spectra below 150 K. The integrated spectral intensity of a 0.9-layer $Fe(CO)_5$ film has been plotted as a function of temperature in the lower portion of Fig. 3. The Mössbauer intensity has a relative minimum near 110 K followed by a maximum at ~130 K in the $\vec{k}_\gamma$ perpendicular configuration with a more rapid decrease in the parallel configuration. This anomalous behavior[17] indicates changes in the Fe mobility *prior* to the OD transition. Although its origin is uncertain, a possibility consistent with the neutron-diffraction patterns is a relative translation of the two monolayer sublattices. That is, the molecule which is slightly off the cell center in Fig. 2(a) (the less favorable site) could commence large amplitude lateral motion about the center position occupied in the orientationally disordered phase.[18]

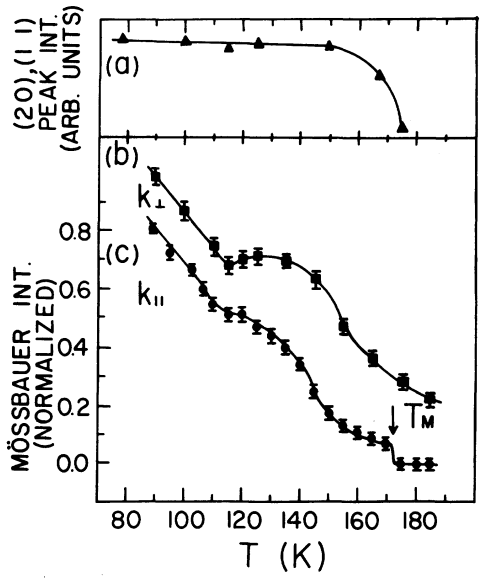

FIG. 3. (a) Integrated intensity of first Bragg peak ($Q = 1.11$ Å^{-1}) vs temperature. Lower portion: temperature dependence of integrated Mössbauer spectral intensity normalized to that at 90 K for (b) $\vec{k}_\gamma$ parallel and (c) $\vec{k}_\gamma$ perpendicular to the Grafoil disks. T_M indicates the melting point of the film. Solid lines in (a), (b), and (c) are guides to the eye.

The OD transition inferred from the neutron-diffraction patterns appears to correlate with an inflection point observed in the Mössbauer intensity at ~150 K in both $\vec{k}_\gamma$ parallel and perpendicular configurations. This is followed by an abrupt drop in intensity near 170 K which is present only in the parallel configuration. This evidence for an enhanced mobility parallel to the surface correlates well with the weakening and broadening of the Bragg peak observed between 167 and 175 K. We conclude that melting occurs at 170 K but considerable short-range order persists in the fluid state.

In summary, we have proposed a herringbone structure for submonolayer $Fe(CO)_5$ on graphite similar to those of N_2 and ethane. The model is consistent with empirical potential calculations, although further confirmation by LEED experiments on a single-crystal substrate would be desirable.[4] Contrary to assumptions of recent computer simulations, Mössbauer spectra indicate changes in the translational mobility of the molecules at temperatures below the OD transition. Above the OD transition, neutron-diffraction patterns are consistent with molecular rotation about the surface normal as assumed in the computer simulations but also suggest coupled translational motion not included in these models. Although we are unable to conclude whether the OD transition is first or second order, the Mössbauer spectra exhibit a more abrupt variation with temperature near melting.

ACKNOWLEDGMENTS

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[11]Due to difficulties in filling the samples (see Ref. 8), the diffraction pattern at 175 K in the fluid phase was used as the background for the patterns at $T \leq 167$ K. The average intensity for $Q < 0.86$ Å^{-1} ($T = 175$ K) was used as background in the region of the first Bragg peak ($0.86 \leq Q \leq 1.40$ Å^{-1}). For the pattern at 175 K which was not analyzed quantitatively, a blank cell containing bare Grafoil was used for the background.

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[13]B. E. Warren, Phys. Rev. 59, 693 (1941).

[14]In the fitting procedure it was necessary to assume a different constant component of the scattering above $Q = 1.8$ Å^{-1} (see Ref. 12). This does not present any problems in determining the integrated peak intensities.

[15]The calculations are similar to those of F. Y. Hansen and H. Taub, Phys. Rev. B 19, 6542 (1979), except that the graphite substrate is now represented by three layers of carbon atoms and the Fe-C interaction is neglected.

[16]Due to steric hindrance, there could be some tipping of the rotation axis away from the surface normal. However, isotropic rotation of the molecule about the Fe atom is unfavorable energetically. The profile calculated for isotropic rotation is indistinguishable from that in Fig. 1 at 167 K.

[17]Earlier results on a Papyex substrate (Ref. 8) showed a monotonic decrease of the Mössbauer intensity in the perpendicular configuration and an abrupt intensity drop near 120 K in the parallel configuration. Although we do not understand these differences between the Grafoil and Papyex samples, both clearly show anomalous behavior in the Mössbauer intensity below the OD transition. Further measurements are in progress (Ref. 10) to clarify the situation.

[18]Such a transition would have little effect on the neutron-diffraction pattern. Occupation of the center site increases the (41) peak intensity, but this could be offset by a Debye-Waller factor contributed by increased translational motion.